

LIMITATIONS ON $\Delta^{17}\text{O}$ AS A TRACER OF PROVENANCE REVEALED BY MINERAL-SPECIFIC VALUES FROM LUNAR AND TERRESTRIAL ANORTHOSITES. Issaku E. Kohl¹, Paul H. Warren, Edwin A. Schauble and Edward D. Young², ¹Department of Earth, Planetary, and Space Sciences, UCLA, USA (ikohl@epss.ucla.edu).

Introduction: Recently published triple-oxygen isotope data from lunar basalts has improved constraints on plausible scenarios for the Moon forming event [1,2]. In these studies extremely high precision $\Delta^{17}\text{O}$ data are presented that in principle would allow for distinguishing materials on the basis of differences of just a few ppm. In order to evaluate the influences of different mass fractionation laws for both Earth and Moon on these results, anorthositic rocks and minerals were measured [1]. While falling within the theoretical envelope for mass fractionation the $\Delta^{17}\text{O}$ values of these anorthositic samples are too low to be explained by differences in mass fractionation laws; the anorthosites have $\delta^{18}\text{O}$ values not far removed from those of their parental material and the fractionation exponents (three-isotope slopes) required to generate the observed $\Delta^{17}\text{O}$ values are far lower than one would expect for igneous processes (Figure 1).

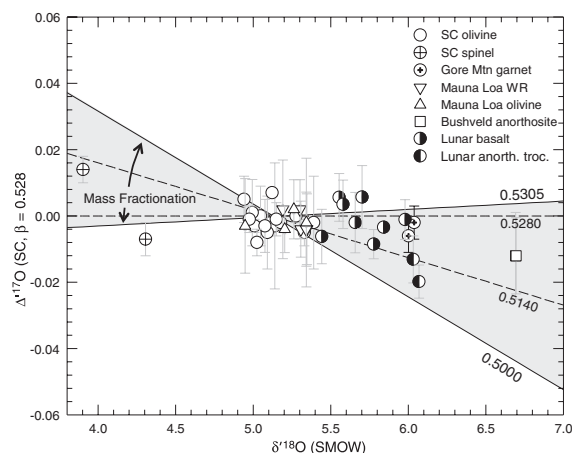


Figure 1. Terrestrial and Lunar oxygen isotope data (from Young et al., 2016). Ordinate is in per mil.

Here we present new data from a larger suite of lunar anorthosites (and anorthositic-troctolites), terrestrial anorthosites, and terrestrial plagioclase separates. These data suggest that rocks dominated by plagioclase, on average, are measurably lower in $\Delta^{17}\text{O}$ than genetically related mafic rocks and minerals. This is shown to be true for both lunar and terrestrial rocks and is difficult if not impossible to reconcile with mass fractionation related igneous processing.

$\Delta^{17}\text{O}$ Reference Frame: We report our data in the San Carlos olivine (SC Ol) reference frame where the

$\Delta^{17}\text{O}$ of SC Ol is taken to be zero, while using SMOW (VSMOW) as the reference for $\delta^{18}\text{O}$. We also select a typical high-temperature fractionation exponent β of 0.528 for our reference. Our use of SC olivine (representing Earth's mantle) as the reference for $\Delta^{17}\text{O}$ at fixed $\delta^{18}\text{O}$ removes any ambiguity surrounding calibrating rock measurements against water. The difficulty of using SMOW when evaluating $\Delta^{17}\text{O}$ of rocks can be seen in disparate results spanning the last decade [3,4,5], resulting in shifts of ~ 50 ppm in the difference between SMOW and SC olivine in just the last several years. For this reason we suggest that using the SMOW reference frame for $\Delta^{17}\text{O}$ of rocks and minerals produces unnecessary chaos in reporting rock data for cosmochemical studies.

Results: The new measurements of lunar anorthosites reported here have an average $\Delta^{17}\text{O}$ of -0.0097% ± 0.002 (1S.E.), or -10 ± 2 ppm (Figure 2). This difference agrees with previously published measurements [1,6] from our lab [1] and from Wiechert et al. [6]. The latter comprise 6 analyses of anorthosites and anorthositic troctolites with an average $\Delta^{17}\text{O}$ of -8 ± 3 ppm, relative to basalts from the same study. The values are $+10$ and $+2$ respectively when normalized to SC Ol and a β of 0.528. These data appear to be the only other published triple-oxygen isotope data for felsic lunar rocks.

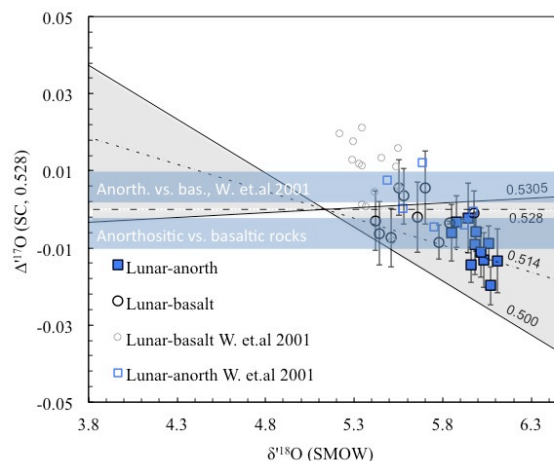


Figure 2. Summary of lunar basalt and anorthosite reported here. Data from [6] are shown for comparison. The ordinate is in per mil. Blue bars reflect the difference in the means.

Plagioclase separates from the Bushveld igneous complex with $\delta^{18}\text{O}$ values of 6.7 and 7.3‰ have $\Delta^{17}\text{O}$ values of -12 and -17 ± 3 ppm, respectively and Lake County plagioclase with a $\delta^{18}\text{O}$ of 5.6‰ has a $\Delta^{17}\text{O}$ of -11 ± 3 ppm (Figure 3). While we are continuing our effort to measure a wider array of plagioclase occurrences with varying An content, the data thus far show remarkable consistency indicating that feldspars are lower in $\Delta^{17}\text{O}$ than other coexisting minerals.

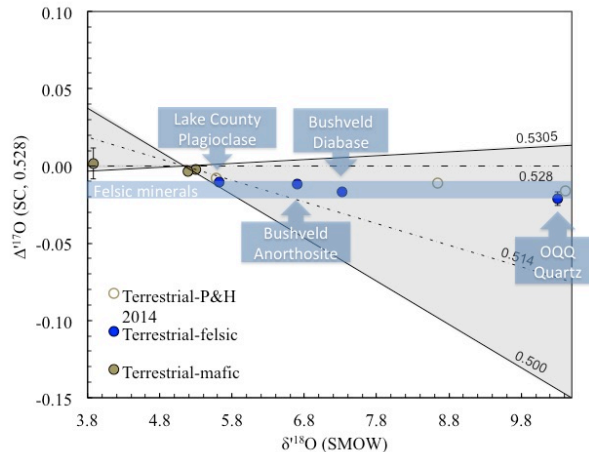


Figure 3. Summary of terrestrial feldspar, quartz and anorthosite data. Ordinate is in per mil.

Mass Fractionation: While we show fields consistent with mass fractionation in Figures 1, 2 and 3 based on the full range of possible values for the three-isotope fractionation exponent β from 0.5305 to 0.500, igneous materials almost always define β values between 0.529 and 0.525. These values, in concert with the small differences in $\delta^{18}\text{O}$ between feldspars and mafic components, are far too high to explain the negative $\Delta^{17}\text{O}$ values of feldspars by fractionation alone (Figures 1, 2, and 3).

We investigated the likelihood that our measured differences derive solely from a mass fractionation effect using *Ab-initio* models for β values. We modeled the oxygen isotope fractionation between anorthite and spinel fractionation relative to forsterite. Anorthite and spinel represents the largest measured difference in our data for both $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$. At igneous temperatures, all mineral-specific β values are > 0.528 . Calculated reservoir effects on effective β values during fractional crystallization are not sufficient to explain the low feldspar $\Delta^{17}\text{O}$ values.

For example, the LMO hypothesis and associated plagioclase floatation mechanism results in anorthosites comprising around 4% of the lunar silicate reservoir [7]. Our modeling suggests that differences in

spinel and anorthite $\Delta^{17}\text{O}$ values are ~ 6 ppm for an anorthositic crust representing 4% of remaining oxygen.

Mg-suite lunar rocks are thought to be the product of later differentiation from a more mafic lower crustal component, which could have experienced prior depletion from its mantle source [8]. Multiple episodes of differentiation resulting in multiple instances of kinetic and equilibrium fractionation are therefore conceivable. These potential “chess moves” in oxygen three-isotope space complicate interpretations. However, even these complicated scenarios do not explain the Bushveld nor the Lake County plagioclase data.

Crystal Chemical Effects on $\Delta^{17}\text{O}$ Values: It is possible that these low $\Delta^{17}\text{O}$ values are specific to tectosilicates lattice structures (see below) and have nothing to do with fractionation. Our *ab initio* calculations are based on harmonic oscillations. The possibility of mineral-specific anharmonic vibrational components cannot be discounted and should be investigated.

Implications: Our observations call into question previous measurements of $\Delta^{17}\text{O}$ measured in felsic plutonic rocks [9] that appear to be indicative of temperature of equilibration.

Our data from Lake County plagioclase show similar $\Delta^{17}\text{O}$ values to those measured in [9] despite much lower $\delta^{18}\text{O}$ values. A single measurement of Oliver Quarry quartz (OQQ) in our laboratory also plots within error of the above datum with $\delta^{18}\text{O}$ of 10.2‰ and $\Delta^{17}\text{O}$ of -21 ± 4 ppm. There appears to be a clustering of tectosilicate $\Delta^{17}\text{O}$ values regardless of source or petrogenetic setting. We suggest that slopes in oxygen three-isotope space are influenced as much by crystal chemistry as they are temperature.

Identification of a crystal-chemical control on $\Delta^{17}\text{O}$ values places important constraints on using triple oxygen isotopes as a diagnostic of provenance in cosmochemistry. Care must be taken to compare crystal-chemically similar materials, for example.

References: [1] E. D. Young, I. E. Kohl, P. H. Warren, D. C. Rubie, S. A. Jacobson, and A. Morbidelli. (2015) *Science*, 351, p. 493 [2] D. Herwartz, A. Pack, B. Friedrichs, A. Bischoff (2014) *Science*, 344, p.1146. [3] M. Kusakabe, Y. Matsuhisa. (2008) *Geochem J.*, 42, p.309 [4] R. Tanaka and E. Nakamura. (2013) *RCMS*, 27(2), p.285. [5] A. Pack, R. Tanaka, M. Hering, S. Sengupta, S. Peters and E. Nakamura, (2016) *RCMS*, 30, p.1495. [6] U. Wiechert, A. N. Halliday, D.-C. Lee, G. A. Snyder, L. A. Taylor, D. Rumble. (2001) *Science*, 294, p.345. [7] G.J. Taylor and M.A. Wieczorek (2014) *Phil. Trans. R. Soc.A*, 372 [8] P.H. Warren, G.W. Kallemeyn. (1990) *J. Geophys. R.*, 98, p.5445 [9] A. Pack and D. Herwartz. (2014) *EPSL*, 390, p.138.

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